Formation of p-n$^+$ diamond homojunctions by shallow doping of phosphorus through liquid emersion excimer laser irradiation

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When processing wide-bandgap crystals with ultrafast laser pulses, the excitation of electrons is initiated through non-linear processes such as multiphoton or tunnel ionization. The electrons can then seed the subsequent electron heating or avalanche ionization, which leads to the efficient absorption of light. With excimer nanosecond lasers, the initial (seed) electrons are mainly generated by the contribution of impurities [1].

Experimentally, the irradiation process is investigated based on diagnostic of time resolved reflectivity as shown in Fig. 1(a) using the experimental setup shown in the inset. With laser irradiation, self-reflectivity begins to increase sharply due to the initial dynamics of the melting process induced by the laser impact with the substrate surface. Owing to ultra-fast electron-phonon energy transfers, an instantaneous and local conversion of the photon energy into heats and pressures is induced. At a low fluence, weak reflectivity implies that the ablation rarely occurs and the irradiated area still retains the higher density of diamond. With increasing laser fluence, the reflectivity is totally enhanced. Reflectivity intensity saturates with the fluence of 5 J/cm^2, which indicates that the ablation process fully occured and the excess laser energy density beyond critical fluence is used to heat the ablated area, consequently raising the peak temperature, resulting in heavier and deeper doping levels. However, due to high thermal conductivity of diamond, the substrate would maintain ablated state for a very short duration of time (almost same as laser duration 20 ns), before ultra-fast quenching, which limits dopant species incorporation depth.

Ablation is further confirmed by modeling of the irradiation process. We assume a melt-interposed transformation schema by employing a spatially selective melting and temperature modeling. Figure 1(b) shows the change in the induced surface temperature at two different fluences confirmming that the photons energy is locally and instantaneously converted into heat. The peak temperarture drastically increases with increasing fluences from 3 J/cm^2 to 5 J/cm^2 to reach extremely high values of almost 4000 °C for single shot at hit point of irradiation, which in turns affects the time at which the surface remains ablated and hence dopant incorporation. Modeling also showed that irradiated areas exhibit same shape and dimensions of the predetermined laser beam profile, and it is mainly affecting the surface layer with penetration depth of only few tens of nanometers as shown in inset Fig. 1(b). This confirms high spatial resolution with minimum stress on the surrounding diamond.

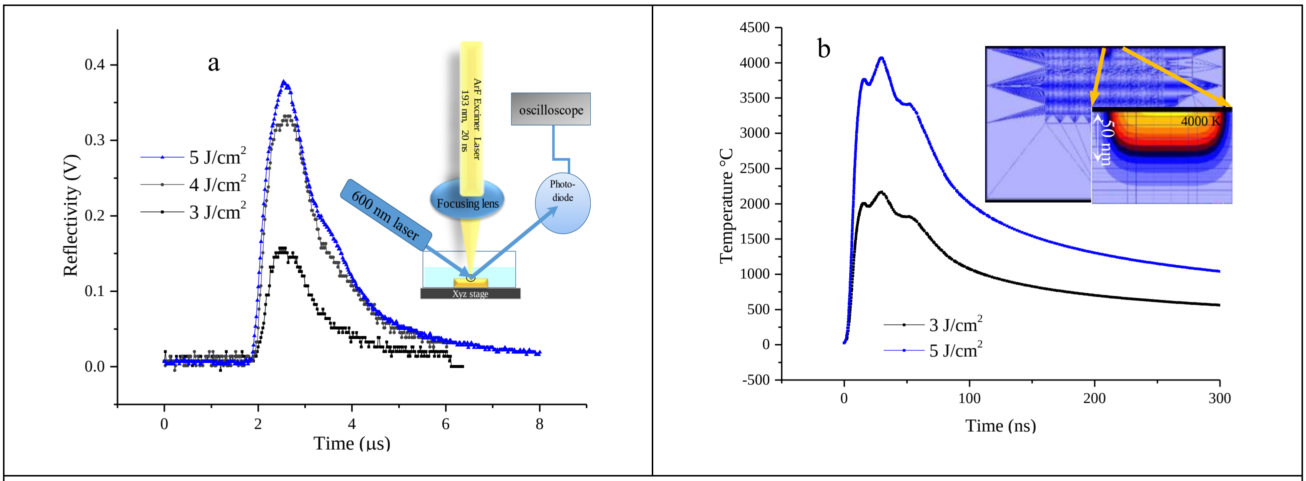

Figure 1. a) Reflectivity from the diamond substrate while irradiating with normally incident ArF laser. b) Process modeling showing induced heat upon irradiation with inset confirming high spatial resolution of the irradiation process.

Crystalline quality of Laser irradiated areas

Employing liquids as a dopant medium during laser irradiation provides higher dopant density to the surface of target material and less induced damages, especially if the liquid retains high viscosity such as phosphoric acid (H_3PO_4 85%). In addition, as it fully covers the diamond substrate, it isolated the sample surface from air, thus reducing graphitization to the minimum. Figure 2 shows Raman spectra for the laser irradiated area on the diamond surface. IT exhibited a sharp peak which come from single-crystal diamond.

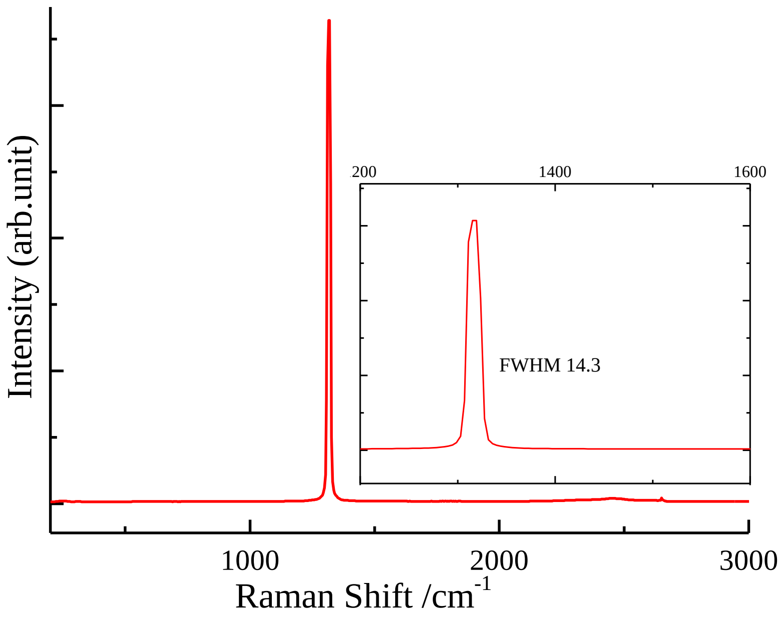

Figure 2. Raman spectrum of laser induced P-doped diamond with inset showing a closer view of the peak FWHM.

The FWHM was increased, mainly due to the strain-induced broadening from the size mismatch between phosphorus and carbon resulting in a slight peak shift as well. whereas any other peaks induced by graphite or amorphous carbon (a-C) are not detected at all. It is known for visible Raman spectroscopy, the sensitivity to sp^2 carbon is an order of magnitude more than that of sp^3 carbon due to the effective excitation of π states by visible photons. Therefore, the absence of G and D peaks in the Raman spectra implies that the irradiated surface spots barely include graphitic amorphous carbon. Consequently, any modifications in diamond characteristics would originate from the incorporation of dopant species. This also implies that the crystalline quality of the induced P-doped layer is the same as that of the diamond substrate, and the incorporation of dopant atoms in the matrix of diamond through laser irradiation did not deteriorate the crystalline quality.

Inclusion of Metal-Assisted Terminated (MAT) layer

MAT buffer layer heavily doped with Tungsten was homo-epitaxial grown by Hot Filament CVD, prior to the drift layer and laser irradiation process for suppression of leakage current. W impurities were generated by direct plasma exposure for the HFCVD film.

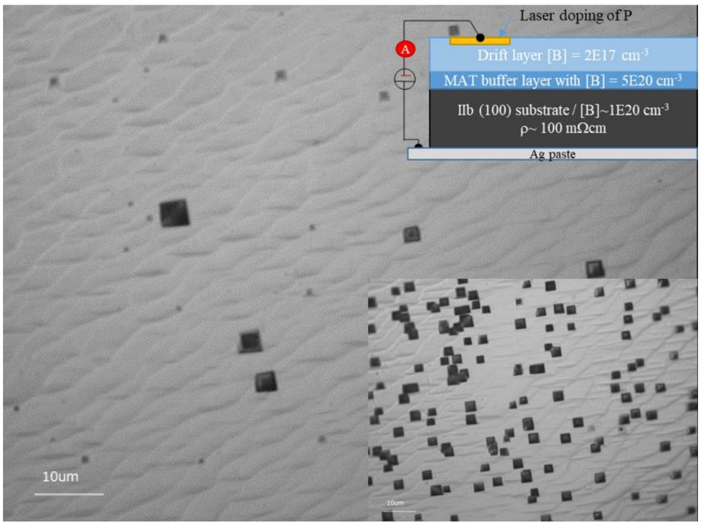

Figure. 3. Etch-pit of the drift layer with inclusion of the MAT layer. Inset shows the drift layer without the MAT layer.

This resulted on a large reduction in the dislocation density and suppress its migration from the substrate to the drift layer as shown in Fig. 3, where dislocation-bundle are greatly suppressed by the MAT buffer layer. This resulted in enhancing device uniformity, ideality factor, and reducing leakage current level. Upon laser irradiation on the substrate and junction formation, the high conductivity of the laser-induced phosphorus-doped layer and high quality of the homojunction formed with less induced defects, further enhanced the device properties. The mechanism of laser-induced doping should be completely different from that of general thermal annealing doping, and it has not been fully clarified yet and further analysis are being conducted. We assumed that during laser induced ablation, the subsurface of the diamond plate is temporally unstable due to thermal expansion, laser-induced shock waves, and vibrational excitations, which generates diffusion paths such as vacancies for dopant atoms. The process showed to enabled selective, fast-patterned doping diamond surfaces. And fabrications of devices that maintain the high purity and durability of synthetic diamond.

[1] Caylar, B., Pomorski, M. & Bergonzo, P. Laser-processed three dimensional graphitic electrodes for diamond radiation detectors. Appl. Phys. Lett. 103, 1–4 (2013).